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TEMPERATURE DEPENDENCE OF LUMINESCENCE IN BERYLLIUM CERAMICS¹

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A relationship is established between x-ray luminescence and variation of the elementary cell parameters of BeO. The lattice deformation and pyroelectric fields lead to the formation of point defects (which are luminescence centers), on which excitons, as well as holes and conduction electrons, are presumably localized.

Ceramic products based on beryllium oxide can find wide application as working bodies for thermally stimulated luminescent and exo-emission dosimeters for ionization radiation.

It is known that low-temperature modification α -BeO crystallizes in a hexagonal syngony and has a wurtzite-like structure with the spatial group $P6_3mc - C_{6v}^4$. Beryllium oxide is a linear pyroelectric with a negative pyroelectric coefficient value within the temperature interval of 4 – 340 K. The effect of phase transitions and pyrofields, which arise in BeO powder monocrystals under temperature variations, on the temperature dependence of the elementary cell parameters was reported earlier [1, 2]. The working bodies of dosimeters made of BeO are subjected to cyclic cooling and heating. The deformation of the crystalline lattice in this case is also accompanied by changes in the temperature dependence of stationary x-ray luminescence (SRL).

It was previously established that the type of temperature dependence of the crystal lattice parameters and luminescent properties of working bodies are related to the average size of BeO microcrystals. The correlation between the temperature dependence of the BeO crystal lattice parameters and SRL of powder and ceramic samples had to be investigated in more detail.

The materials investigated were BeO powder with a mean size of microcrystals of 2.5 – 3.0 μm and sintered ceramics with particles sized 30.0 – 40.0 μm . Variations in the elementary cell parameters of microcrystals in BeO powder under cooling and heating were investigated (Fig. 1). It can be seen that variation of the elementary cell parameters a_0

and c_0 is rather complex and is accompanied by hysteresis. Immediately after a heating – cooling cycle, the values of a_0 and c_0 at 300 K (Fig. 1, points a and c) did not coincide. Exposure of the samples (at 300 K) in air for 40 min led to increasing a_0 and c_0 (Fig. 1, points b). On further exposure of the samples for 1 h, the parameters returned to their initial state (Fig. 1, points a). In cooling beryllium oxide ceramics (Fig. 2), different variations of a_0 and c_0 than in BeO powder were registered. It can be assumed that this fact is related to the average size of the BeO microcrystals. It is probable that the temperature dependences of the a_0 and c_0 variations are somehow influenced by thermal stresses arising as a conse-

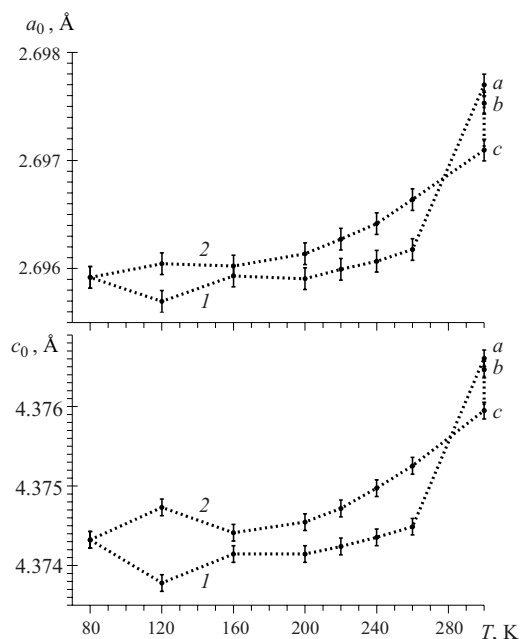


Fig. 1. Variation in elementary cell parameters of BeO crystals in powder under cooling (1) and heating (2).

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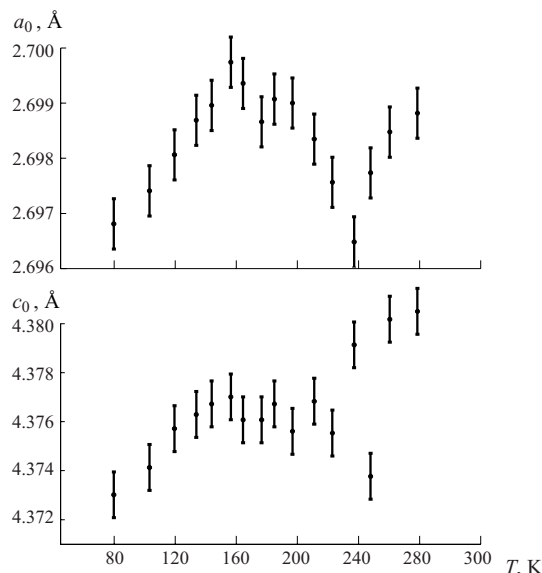


Fig. 2. Variation in elementary cell parameters of crystal beryllium oxide ceramics under cooling.

quence of the rigid fixation of BeO microcrystals in ceramics. Such an influence in fine powder ought to be minimal. Thermal stress probably generates point defects.

It is known that luminescence of BeO excited by x-ray radiation and electrons has the most intense peaks at 4.9 and 6.7 eV. The present study investigated the temperature dependence of SRL of the peak at 4.9 eV in powders and ceramics.

Figure 3 shows temperature dependences of SRL of powder and beryllium ceramic samples under cooling and subsequent heating. The curve of the temperature dependence of SRL in cooling does not coincide with the heating curve. Similar correlations were identified for powder and ceramic samples under excitation of luminescence by short electron pulses.

An electric field in pyroelectric materials significantly depends on the shape and size of the crystals. In the largest BeO crystals (greater than 30 μm), the pyroelectric field, when temperature changes, injects charged electrons and ions along the polar axis (axis C). Localization of particles in the crystalline lattice of BeO creates a volume charge, which intensely deforms the dipole element of the polar matrix, namely, oxygen tetrahedrons $[\text{BeO}_4]$. The process of heating and cooling of BeO crystals within a sufficiently wide temperature interval is related to numerous transitions of Be^{2+} ions into interstices inside the cation sublattice (a blurred phase transition).

Thus, a temperature variation in BeO microcrystals is accompanied by a variation in the crystal lattice parameters a_0 and c_0 . This is especially typical of c_0 : the larger the size of the BeO crystal, the more perceptible the variation of c_0 .

Anomalies of physicochemical properties in pyroelectric crystals [3] are determined both by processes in the electron

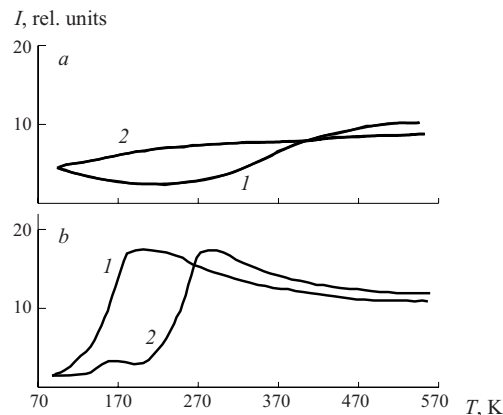


Fig. 3. Temperature dependence of stationary x-ray luminescence of samples of powder (a) and beryllium ceramics (b) under cooling (1) and subsequent heating (2).

or photon subsystems and by different distributions of impurity atoms by possible states as temperature changes. Gurevich and Kharkats [4] attribute an abrupt disordering of one of the ionic sublattices in crystals to the formation of phase transitions of the first kind. Pyrofields are capable of modifying the point symmetry of BeO crystals and also result in the formation of point defects.

The luminescence band at 4.9 eV is complex and consists of at least four overlapping bands. There are several hypotheses on the origin of SRL of this band, which is presumably due to several luminescence mechanisms simultaneously. Among the latter one can distinguish luminescence of impurity centers and color centers (F^- and F^+ centers), radiation recombination of electrons with holes localized on defects and holes with electrons localized on defects, as well as luminescence of free and autolocalized excitons. According to the data in [5], luminescence at 4.9 eV is determined only by radiating annihilation of free and autolocalized excitons. It is established [6, 7] that luminescence of ceramics is also related to impurities located on the surface of microcrystals and pores, which isomorphically replace Be^{2+} ions in the cation sublattice and lead to the formation of mechanical stresses in crystals. The study in [7] discusses the role of oxygen vacancies, which have an effect on BeO luminescence and result in the formation of F^+ centers.

Thus, the temperature dependence of stationary x-ray luminescence in beryllium ceramics is related to variations in the elementary cell parameters of BeO and is determined by the size of the microcrystals and, presumably, by the parameters of pyroelectric fields arising inside the microcrystals under cooling and heating and to dynamic specifics of the crystal lattice of BeO. The deformation of the lattice and the pyroelectric fields leads to the formation of point defects (which are luminescence centers), on which excitons and also holes or conduction electrons are probably localized.

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